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Decr. 26. 1873.

J. F. Campbell

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ON THE OCCURRENCE OF SILICEOUS NODULAR BROWN HÆMATITE (GÖTHITE), IN THE CARBONIFEROUS LIMESTONE BEDS NEAR COOKSTOWN, CO. TYRONE; AND NOTE ON ITS FORMATION BY CHEMICAL ALTERATION FROM ORDINARY CLAY-IRONSTONE. WITH ANALYSIS.[1]

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THE ore which is the subject of this paper occurs in rather an uncommon manner; its existence, however, has been known for a very considerable period, and it is said to have been worked at least 250 years ago. I believe it is this that is referred to in Dr. Boate's quaint work, "Ireland's Naturell History,"[2] as being found "by the side of the rivulet Lishan, not far from Lough Neagh,"—although he classes it with the ordinary clay-ironstones, which it certainly does not resemble either in composition or appearance.[3]

It is found at a place called Cove Bridge, near Lissan, in the townlands of Unagh and Tullycall, about two miles north-west of Cookstown. Here there are numerous traces of old workings, and in the rivulet which separates the townlands, as well as in various quarries and rock exposures hard by, sufficient evidence is to be had to enable one to determine with tolerable exactness the position and mode of occurrence of this singular deposit. The section shows a succession of beds of coarse and fine, yellow, purple, and reddish sandstones and grits,—passing into quartzose conglomerate,—interstratified with variously-coloured sandy and clayey ferruginous shales, and several limestones, marbly and dolomitic, closely resembling some of the Armagh beds. In the shales are hollow nodules of hæmatite, sometimes very sparingly distributed, but in at least one bed very abundant. This bed, I am informed by the men who had proved it,—for it does not appear at surface,—is 4 ft. 6 in. thick, the shale, which is itself highly ferruginous, being crammed with nodules, and it has been worked to some little extent. Two pits were opened on it about eighteen months ago; but, as in all mines of this kind, they were found difficult to keep in order, and therefore dangerous to work, and the miners took fright and gave up the attempt.

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[1] Read before the Royal Geological Society of Ireland, May 14th, 1873.

[2] Published in 1652.

[3] It is also referred to by Sir Richard Griffith in his Catalogue of Fossil and Mining Localities, Journ. Geol. Soc. Dublin, vol. ix., and its position marked on his Map; and it is mentioned in Portlock's "Geological Report on Londonderry," etc.; but, so far as I am aware, has never been described before.

The following is a section of the strata in which the ore lies, compiled partly from information and partly from my own observation, commencing at the top with the beds passed through in the pits above referred to. (See Sketch Section, p. 7.)

SECTION NEAR COVE BRIDGE.

				Feet	in.
	11	Drift, etc., and	about	55	0
Probably Lower Carboniferous Beds.	10	Shale (a couple of feet thick) with some hæmatite nodules			
	9	Coarse rotten sandstone		3	0
	8	Red clayey ferruginous shale, full of hæmatite nodules. (Workable bed.)		4	6
	7	Whitish sandstone, about		2	0
	6	Hard reddish quartzose conglomerate (calcareous)		1	6
	5	Rotten yellow decomposed clayey sandstone		2	0
	4	Reddish shale, with hæmatite nodules		1	0
	3	Yellow and brown sandy clay, with occasional hæmatite nodules		2	0
	2	Purple, grey, and marbly massive limestone		8	0
	1	White, yellow, and purple coarse grits and sandstones, streaked. Thickness not seen			
				79	0

It is probable that over these, other workable beds of ore must exist, because the mass of old workings are some distance to the dip of this place, and it is not at all likely that the ancient miners would venture to a depth sufficient to catch the 4 ft. 6 in. seam there.

The above section is only approximately correct, as the junction of some of the beds is not visible. The relative position of the strata can, however, be distinctly traced, and the interstratification of the ore-filled shales fully made out. They do not, like others of the kind, lie in veins, pockets, or erosions in the limestone. In one place, indeed, there is a slight depression in the limestone under the shale, but it is difficult to say whether it is due to erosion or to a small fault.

The nodules are mineralogically very peculiar. They are usually in the form of a hollow shell, of, say, a quarter inch in thickness. The greater part of this is made up of a very hard compact siliceous brown hæmatite, of a dark brown colour, but the interior is covered with a thin coating of fibrous and mammillated limonite (Fig. 2 *b*). When they are found *in sitû*, and perfect, they often contain a kind of nucleus of sandy shale or clay. (See Woodcut, p. 7.)

The shale in which they occur is generally ochreous red, and seems to be highly ferruginous. Being apparently very aluminous, as well as in parts calcareous, it might be advantageously used as a flux for the ore were it worked. In this way the whole bed might perhaps be utilized.

That the ore is of excellent quality for the smelter will be perceived from the following analysis. The specimens used were taken at random from a large heap left after the new workings were discontinued, and were not the very best,* for those had been taken away before, and Dr. Ritchie, of Belfast, informed me that some he had estimated yielded over 60 per cent. of iron.

ANALYSIS OF ORE.

Fe_2O_3	74·56	H_2O (Hygroscopic)	2·90
FeO	a trace	MnO_2	a trace
MgO	0·044	CO_2	a trace
CaO	a trace	P_2O_5	a trace
SiO_2 etc.	9·42†		
Al_2O_3	3·51		100·674
H_2O (combined)	10·24	Metallic Iron = 52·20	

This seems to give the composition of Göthite, $Fe_2H_2O_4$,‡—a metahydrate which is a usual form of brown hæmatite,—together with a hydrous silicate of alumina, such as Kaolin, and some free silica. It might be nearly represented by the formula—

$$\underset{\text{Göthite.}}{14Fe_2H_2O_4} + \underset{\text{Kaolin or Clay.}}{Al_2Si_2O_7 2H_2O} + \underset{\text{Silica.}}{2SiO_2}.$$

There was a total absence of sulphur, and the merest trace of phosphoric acid could only be detected by the most delicate test: thus the ore is extremely well suited for the manufacture of Bessemer steel. For a brown hæmatite the per-centage of iron is very high; and from its composition it seems to be well adapted for admixture with clay-ironstones, or with the aluminous ore of Antrim. As to its extent, it may run for a considerable distance to the south-east; and if the thickness and richness hold good, it may prove to be a very valuable deposit.

By the kind permission of Prof. Galloway the analysis was made in the Laboratory of the Royal College of Science, Dublin.

It appears to be a circumstance of some novelty to find an ore of this kind as a bed, or part of a bed, in the Carboniferous Limestone, and interstratified with the rocks of that formation. In the North of England, where very extensive deposits of red and brown hæmatite are worked in the limestone, their true mode of occurrence is very doubtful, and for the most part it is believed that they either lie in cavities of erosion in the limestone, or in veins and lodes.[1] In the Alston Moor district, however, brown iron ore occurs associated with the beds of clay-ironstone lying between the "Great" and "Little" Limestones, but it is considered to have some relation to the veins which traverse the country;[2] and although at Cleator, in the Whitehaven district, red hæmatite is found apparently interbedded with shale and conglomerate, this seems to be thought by no means proved.[3] In at least one locality in England hæmatite has been found unmistakably interbedded with the Carboniferous rocks. Its position is given in a section of part of the Old Red Sandstone and Carboniferous Rocks of Lower Purlieu, Forest of Dean, Gloucestershire, in Sir Henry De la Beche's Memoir on the Formation of Rocks in South Wales and South-Western England.[1] The section is chiefly made up of sandstones, shales, and limestones, like that at Cookstown, and, massed together, is as follows:—

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* I found even better specimens, in appearance, in the thin shale-beds.

† Soluble silica, together with the insoluble residue, containing a little alumina.

‡ Manual of Geology (Jukes and Geikie), p. 63.

[1] Iron Ores of Great Britain, part i. p. 14, W. W. Smyth (Mems. Geol. Surv. of Gt. Brit.).

[2] Iron Ores of Great Britain, part i. pp. 14–17.

[3] *Op cit.* pp. 20–23.

	Feet.
Sandstones and Shales	88
Limestone	90
Limestone with intermingled hæmatite, extensively worked... ...	60
Limestone	330

Sir H. De la Beche considers the occurrence of the ore, in beds, very unusual in the Carboniferous Limestone.

The above account, however, does not state in what form the hæmatite is found, whether in nodules, or amorphous or crystalline layers, and in fact in only two instances can I discover any definite account of an iron ore existing in any quantity in the form under notice. It appears that in the Lower Greensand at Seend, near Devizes, and also in Buckinghamshire, nodules of limonite, often hollow, and filled with white sand, are found in thick brown sand. The composition of that at Seend somewhat resembles that of the Cookstown ore.[2]

A similar ore occurs associated with the clay-ironstones of the Dungannon Coal-field, and in its analysis as given by Sir Robert Kane,[3]—who says that it has been found in abundance—the resemblance is very close. A specimen I picked up at an old pit there was extremely like it, containing also a sandy nucleus; but after many searches I was unable to find any others.

This brings us to one of the most interesting points about the ore, namely, the mode of its formation. I believe it may be considered a kind of pseudomorphic product, the result of the chemical action of water carrying various substances in solution, on nodules of clay-ironstone, the former occupants of these shale-beds; and in order to arrive at the present state of the mineral, we must understand three distinct processes to have taken place. The clay-ironstone nodules, of which numbers are found in the shales of the Carboniferous rocks of the district, were first formed in the usual way by segregation of the highly ferruginous particles of the clays, etc., in which they occur. Then, in the course of time, water passing through the diversely constituted rocks overhead, and therefore taking up alkaline silicates, carbonic acid, bicarbonate or hydrate of lime, sulphate of lime, and of course carrying oxygen, would gradually, by a long series of rather complex decompositions, completely or in part alter the clay-ironstone.

The carbonate of iron might undergo alteration by several reactions, the simplest of which would be by the direct effect of oxygen, thus:—

$$\underset{\text{Carbonate of Iron.}}{4FeCO_3} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Göthite.}}{2Fe_2H_2O_4} + \underset{\text{Carbonic Acid.}}{4CO_2}$$

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[1] Memoirs Geol. Surv. Great Britain, vol. i. pp. 128–130.

[2] Bauerman's Metallurgy of Iron, p. 76. Contains very little alumina, but much silica.

[3] "Industrial Resources of Ireland," p. 129.

And the carbonic acid thus set free would no doubt re-act on a portion of the proto-silicate of iron also contained in clay-ironstone, producing a fresh supply of carbonate of iron, to be again decomposed, as in the above equation:—

$$\underset{\text{Proto-silicate of Iron.}}{Fe''_2SiO_4} + \underset{\text{Carbonic Acid.}}{2CO_2} = \underset{\text{Carbonate of Iron.}}{2FeCO_3} + \underset{\text{Silica (free).}}{SiO_2}$$ [*]

By another series of re-actions the clay or silicates of alumina would be decomposed, but would be carried off in solution. The removal of these substances may be accounted for in several ways.

(1). Silicates of alumina are decomposed by sulphate of lime, forming sulphate of alumina—-which is soluble—and silicate of lime: [†]

$$\underset{\text{Kaolin or Clay.}}{4(Al_2Si_2O_72H_2O)} + \underset{\substack{\text{Sulphate}\\\text{of Lime.}}}{6CaSO_4} = \underset{\substack{\text{Sulphate}\\\text{of Alumina.}}}{2Al_2(SO_4)^3} +^{‡} \underset{\substack{\text{A double Silicate}\\\text{of Lime and Alumina}\\\text{on Garnet type.}}}{Ca_6Al_4(SiO_4)^6} + \underset{\text{Water.}}{8H_2O} + \underset{\text{Silica.}}{SiO_2}$$

The silicate of lime would then be decomposed by carbonic acid,[§] carbonate of lime being formed as already shown (see note *antè*), and would be carried off by the acid water.

(2). When alkaline silicates are allowed to act on silicates of alumina, they extract minute quantities of alumina; and silicate of soda possesses this property to a very sensible degree: moreover, the alkaline silicates dissolve small portions of the silicate of alumina itself.[‖] Thus in time a considerable quantity of alumina might be removed.

Now all these are solutions we should expect to find in the vicinity of strata made up of calcareous and arenaceous rocks. It is of course well known that the water of limestone districts often contains a large amount of sulphate of lime, to which is due what is called its "permanent hardness"; on the other hand, the solution of alkaline silicates may result from the action first of carbonic acid on minerals containing them, and then the subsequent re-action of the alkaline carbonates so obtained on silicate of lime.

By these agencies then, (1) and (2), the silicates of alumina forming the clay must have been for the most part extracted. It will be hardly necessary to remark that carbonic acid would have no direct effect on them, as it does not combine at all with aluminium.

Thus the clay-ironstone results in brown hæmatite more or less free from siliceous and clayey particles, according to the extent to which the alteration has been carried. The final process seems to have been the deposition from solution of the thin external layer of pure fibrous hydrate.

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[*] See Bischof's Chem. Geol., vol. ii. pp. 59 and 61. A similar re-action is given in vol. i. p. 2, solid silicate of lime in water containing carbonic acid gives carbonate of lime and free silica. The equation is my own—

$$\underset{\text{Silicate of Lime.}}{Ca_2SiO_4\,(?)} + \underset{\text{Carbonic Acid.}}{2CO_2} = \underset{\text{Carbonate of Lime.}}{2CaCO_3} + \underset{\text{Silica.}}{SiO_2}$$

[†] Bischof's Chem. Geol., vol. ii. p. 68.

[‡] This formula is merely intended to represent graphically what might take place, but by no means to assert the constitution of the body formed.

[§] Also by alkaline carbonates, by which the silica as well would be removed.

[‖] Bischof's Chem. Geol., vol. ii. p. 66.

While it is thus shown how such a change is theoretically possible, it is satisfactory to obtain undoubted evidence that this metamorphosis of clay-ironstones of various kinds really does take place; and it may, I think, be proved pretty conclusively by the following example.

On the southern shore of Lough Neagh is found a great thickness of beds of—sometimes very arenaceous—pottery clays, with sand, and occasionally beds of lignite, besides concretionary sandstones, and nodules of clay-ironstone. The whole has been correlated with the Bovey Tracey deposit, but is, I believe, of somewhat more recent date. The ironstones are very hard and compact,[1] sometimes of a slightly greenish colour, and seem to consist chiefly of proto-silicate and carbonate of iron; but the outside is often composed of a thick crust of hard, close, siliceous brown hæmatite, evidently the fruit of the chemical alteration of the original nodule. One of them is represented in the accompanying Woodcut (see Fig. 3). The external shell of hæmatite (*b*) is nearly a quarter of an inch thick, and it almost completely incloses the unaltered ironstone, being broken to show the interior. A qualitative examination was made by me of a portion of the unaltered part of one of these nodules with the following result.

It did not effervesce at all with dilute acid; but when powdered, and treated with strong hydrochloric acid, and gently heated, violent action took place, and much carbonic acid was given off. The insoluble residue, consisting chiefly of silica, alumina, and a little protoxide of iron, was not unusually large compared with the bulk taken. The solution contained a very large amount of protoxide of iron, with alumina, and a trace of peroxide of iron. Only a very small trace of lime could be discovered; nothing else was looked for. Tabulated ~~Translated~~ for the sake of clearness, this gives—

$SiO_2 + Al_2O_3$ etc.	(insoluble residue).
Fe_2O_3	a trace.
FeO	in large quantity.
Al_2O_3	
CaO	a trace.
CO_2	in large quantity.

It was not considered necessary to make a quantitative examinaion; for the above could leave no doubt as to the composition of the nodule. It is a clay-ironstone, made up of carbonate of iron, proto-silicate of iron, and clay, or silicate of alumina.

These specimens are therefore useful in placing before us the exact method of transformation of clay-ironstone into nodular hæmatite. It is only by the infiltration of water containing oxygen and other chemical agents that these could have been effected, for ordinary atmospheric air could have had no access to them, some of these Tertiary ironstones having been got from beds of clay 20 feet thick, and often covered by from 10 feet to 30 feet of glacial drift. Indeed, the effect of the atmosphere would be merely to form a thin

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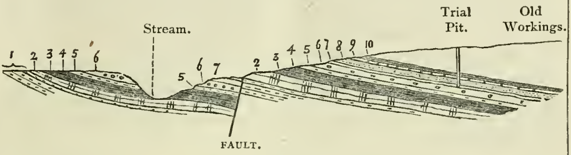
[1] They contain reed-like plants, still retaining the woody tissue.

FIG. 1.—SKETCH SECTION,

To show mode of occurrence of the Hæmatite deposit in the Carboniferous Limestone Beds near Cookstown, Co. Tyrone.



Longitudinal Scale, twelve inches to one mile.
Vertical Scale, about 240 feet to one inch.
Thickness of beds much exaggerated.

(Details of Section will be found at p. 2.)

FIG. 2.

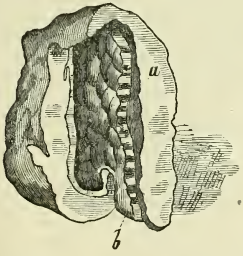
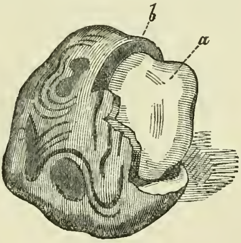


FIG. 3.



About half the natural size.

FIG. 2.—Hollow nodule of brown Hæmatite from shale beds near Cookstown.
- (*a*) Shell of compact Hæmatite.
- (*b*) Internal coating of mammillated fibrous brown Hæmatite.

FIG. 3.—Nodule of Ironstone from later Tertiary beds of Lough Neagh; partially altered.
- (*a*) Original Clay-ironstone forming interior nucleus.
- (*b*) Shell of pseudomorphic brown Hæmatite consequent on decomposition of (*a*).

crust of brown oxide which would not be likely to consolidate, but would be removed almost as soon as formed by the weather.[1]

It seems worthy of remark, however, that these Tertiary ironstones are very nearly as fully developed, both in their original and metamorphic stages, as their more ancient brethren of the Carboniferous period. And it appears, that just as we have perfectly consolidated rocks of all ages, so with the power of water to produce complicated changes on all rocks through which it may be able to percolate, even when they are in part composed of constituents apparently so unsusceptible to its influence, or belong to a period that may be called the yesterday of Geological history.

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[1] The appearance of clay-ironstones which have been exposed to the weather for a long period is very different from that of any of these; and the thin crust of very incoherent oxide is more highly hydrated, its composition being $Fe_4H_6O_9$.—Manual of Geology (Jukes and Geikie), pp. 15 and 23.

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